REPORT D	OCUMENTATION PA	GE Al	FRL-SR-BL-	ΓR-99-
Public reporting burden for this collection of informathe data needed, and completing and reviewing this reducing this burden to Washington Headquarters	ation is estimated to average 1 hour per response, ir s collection of information. Send comments regarding Services, Directorate for Information Operations and	ncluding the time for reviewing this burden estimate or a	000	ining for
Management and Budget, Paperwork Reduction Proceedings 1. AGENCY USE ONLY (Leave blank)	oject (0704-0188), Washington, DC 20503  2. 1/11/99	3. FINAL TECHNIC 9/1/95 - 8/	31/98	· · · · · · · · · · · · · · · · · · ·
4. TITLE AND SUBTITLE			5. PE - 61103	BD
(U) AASERT95/Science and I Combustion and Propulsion	Engineering Training in		PR - 3484 SA - WS G - F4920	-95-1-0406
6. AUTHOR(S)				
I. GLASSMAN	ı			
7. PERFORMING ORGANIZATION N	NAME(S) AND ADDRESS(ES)		8. PERFORMIN	G ORGANIZATION
PRINCETON UNIVERSITY DEPT. OF MECHANICAL & AEROSPACE ENGINEERING PRINCETON, N.J. 08544			REPORT NU	MBER
9. SPONSORING/MONITORING AG	ENCY NAME(S) AND ADDRESS(ES)			NG / MONITORING
AFOSR/NA 801 North Randolph Street Arlington, VA 22203-1977			AGENCY H	EPORT NUMBER
11. SUPPLEMENTARY NOTES			<u> </u>	CENTRAL CONTRACTOR CON
12a. DISTRIBUTION/AVAILABILITY Approved for public release; dis				12b. DISTRIBUTION CODE
13. Abstract (Maximum 200 words	)			
AASERT support per Research" program at Prince sub and supercritical condit enormous success. It was for exponential rate A factor ord the complete energy range to fuels studied, cyclic hydroca	rmitted an additional graduate eton. This support allowed for ions. This newly integrated p ound that under supercritical der of magnitudes greater tha ested remained the same. For arbons formed under supercritical clear aromatics (PAH) that are	uel pyrolysis and corogram, with AAS conditions the pyron results obtained urther, due to the pitical conditions, b	ombustion to ERT support, rolysis rate of at 1 atm. The henomenon k out not at 1 atr	be studied under both proved to be an fuels have a pre- e activation energies of mown as "caging" for the n, and these cyclic
14. SUBJECT TERMS			1	15. NUMBER OF PAGES
14. SUBJECT TEMMS				12
Graduate Student Supp	oort – Supercritical hydrocart	on fuel		16. PRICE CODE
17. SECURITY CLASSIFICATION Unclassified	18.SECURITY CLASSIFICATION OF THIS PAGE Unclassified	19. SECURITY CLASS OF ABSTRACT Unclassified	SIFICATION	20. LIMITATION OF ABSTRACT UL

For BANK Same

## FINAL REPORT AASERT GRANT

(AFOSR GRANT F49620-95-1-0406)

Principal Investigator: I. Glassman

Department of Mechanical and Aerospace Engineering

Princeton University

Princeton, NJ 08544

### A. Summary

The ASSERT supported graduate students had worked on the investigation of the thermal and combustion characteristics of fuels at conditions of special interest to the Air Force. The efforts had concentrated on the characteristics of endothermic fuels necessary as coolants in next generation aircraft and fuel fouling under sub- and super-critical conditions. The students are presently writing their Ph.D. thesis.

### **B.** Technical Discussion

Princeton's efforts in its AFOSR research program, "Fuels Combustion Research" (AFOSR Grant F49620-98-1-0134) concentrated on the pyrolysis and combustion of endothermic fuels under subcritical conditions and the pyrolysis of the same endothermic fuels and components of JP fuel under supercritical conditions. The motivation for the new approach in this program had been the Air Force's interest in advanced cooling techniques for high speed aircraft and its plan for the next generation aircraft gas turbines whose compression ratios would be increased to the extent that the fuel lines feeding the combustors would enter the supercritical range. This new motivation led to an integrated research effort under AFOSR's Princeton grant to study in detail the pyrolysis and combustion of methylcyclohexane (MCH) and decalin at 1 atm pressure and the pyrolysis of these fuels and tetralin under supercritical conditions. The experimental approach required continuation of 1 atm studies in the Princeton Turbulent Flow Reactor, which have been described in numerous AFOSR progress reports and archival papers (1-4) and the development of a unique, new supercritical flow reactor (5-7). The new supercritical experimental work required the addition of another graduate student to the program. Since support of graduate students had been one of the major contributing costs to the budget of the primary AFOSR program, it would have been impossible to add another student to the effort

because of cost limitations. The awarding of the AASERT Grant that is the subject of this final report made it possible to enlist a new student, pursue the supercritical efforts and make some significant contribution to the understanding of the pyrolysis of aircraft fuels under supercritical conditions.

The overall approach allowed by the AASERT grant of having different students working in different pressure ranges with the same fuels had proved to be an enormous success. The global kinetic rates of MCH, decalin and tetralin for their first order decomposition were determined. Figure 1 summarizes the kinetic results at both 1 atm and the supercritical condition of 45 atm and Figure 2 reports the kinetic rate constants and major products found under these two different pressure conditions. These results were obtained from detailed experimental chemical analysis and for the supercritical case from numerous histograms typified by Figure 3. The significance of obtaining histograms of the type represented by Figure 3 is worth emphasizing. All the supercritical results were obtained by the graduate student supported by this AASERT Grant.

To be noted in Figure 2 is that dimethylcyclopentane is not formed in the 1 atm studies with respect to methylcyclohexane and methylhexahydroindane is not formed in the 1 atm studies of decalin. If one examines the activation energies of all systems reported in Figure 2, one notes that all except the subcritical study of decalin are in the 270 kJ/mole range. The statistical analysis of the experimental subcritical results requires reporting the results stated; however, since all the other results report values around 270 kJ/mole, one would expect similar initial bond breaking under the subcritical decalin condition compared to the other cases and thus one would expect that the true experimental activation energy value would also be in the 270 kJ/mole range. This modification is significant in that to keep the actual energy values within the proper range the pre-exponential A factor would have to be of the order 10<sup>13</sup>sec<sup>-1</sup>, as exists for the subcritical results for methylcyclohexane. The significance is that then the subcritical results report an A factor of 10<sup>13</sup>sec<sup>-1</sup>, the supercritical results report an A factor of 10<sup>15</sup>sec<sup>-1</sup> and all the activation energies are essentially similar. This two order of magnitude difference in the A factor may be significant.

The subcritical (gas phase) methylcyclohexane pyrolysis results revealed that methylcyclopentane pyrolysis was to be  $\beta$  scission dominated and, little, if any, PAH is found during the pyrolysis. The major pyrolysis products were ethene, 1,3 butadiene, methane and propane. It has been concluded that under supercritical conditions while  $\beta$  scission processes are still important, they are significantly slower at 1 atm. Further, dimethylpentane and methylcyclopentane are major products not found under subcritical conditions (Fig. 2). Thus, it

had been proposed that dimethylpentane develops from an intermediate methylhexedienyl radical (MHDL). The process by which the initial 6-member ring is converted to a 5-member ring is most apparently due to the phenomenon of caging, a phenomenon frequently discussed in the supercritical chemical process literature<sup>(8)</sup>.

Thus, it appears quite evident that under supercritical conditions, methylcyclohexane pyrolysis creates MHDL which then follows two possible routes to further change:  $\beta$  scission leading essentially to innocuous products or a cyclization due to the phenomenon called caging and possibly leading to significant PAH formation. Obviously, the extent of either route depends on the physical parameters of the set of experiments reported in Figs. 1 and 2.

To understand the phenomenon of caging, it is best to consider both routes simultaneously. To offer a simple phenomenological approach, consider that in the dissociative  $\beta$  scission process, the products of any  $\beta$  scission step must diffuse away in competition with a collision process that would cause a radical such as MHDL to form a new bond instead of breaking one and create a cyclohydrocarbon compound. One can visualize that this process would most likely occur under very high pressures. Thus it is quite apparent that in a practical system the amount of PAH and subsequent particulates that form are due to the competitive "rate processes", one controlled by the diffusion of dissociated species ( $\beta$  scission) and the other by a collision rate process that forms a new bond (caging).

In order to estimate the effect of caging with respect to a chemical process, the general approach had been to apply transition state theory  $^{(8,9)}$ . What essentially has been considered is the rate of formation of a product through an intermediate (complex) in competition with the intermediate reforming the initial reactant. However, Princeton's work with respect to pyrolysis has extended the concept in that the intermediates do not proceed back to the reactant, but have two possible routes to form different products, one a  $\beta$  scission route to innocuous products and the other a caging process leading to products which could cause fuel line fouling.

Now, following the classical chemical approach to evaluating the extent of a given route, the argument has been presented that under supercritical conditions the extent of PAH formation would be determined by the ratio of the collisional rate of formation of the new cyclohydrocarbon due to caging to the diffusion rate of the  $\beta$  scission products "to get out of the cage". This ratio can be represented by the following expression

$$\frac{vd^2 \exp(-E/RT)}{D} \qquad \text{or} \qquad \frac{v \exp(-E/RT)}{\left(D/d^2\right)}$$

where v is the crossing frequency (sec<sup>-1</sup>),  $d^2$  the collision cross section, E the activation energy and D the mass diffusivity  $(cm^2/sec)^{(8)}$ . Essentially  $vd^2$  is the pre-exponential kinetic A factor of the rate expression in the numerator. The second representation above is formulated so that a ratio of characteristic times is presented. This time rate will be recognized as a Damkohler number<sup>(8)</sup>. Further, for the pyrolysis processes under consideration in this effort, the caging institutes a bond formation process and thus the activation energy is zero. The relevant Damkohler number is then  $[v/(D/d^2)]$ .

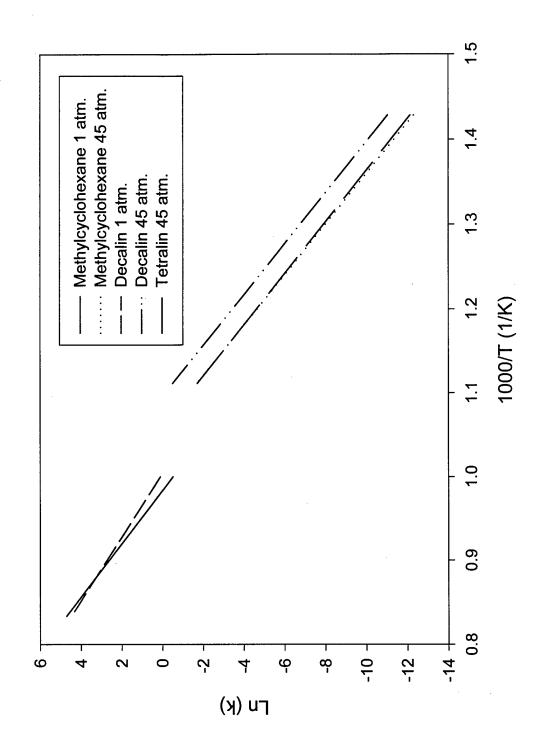
Typical small molecular diffusivities have been reported to be from 10<sup>-1</sup> cm<sup>2</sup>/sec for gases to 10<sup>-5</sup> cm<sup>2</sup>/sec in liquids<sup>(8)</sup>. One would estimate that under the supercritical conditions of the experiments discussed here that the diffusivities of a supercritical fluid would be somewhere between the two values, say of the order 10<sup>-3</sup> cm<sup>2</sup>/sec. It is very tempting to speculate that the two order of magnitude differences in A factor found between the subcritical and supercritical conditions reported in this research is due to two orders of magnitude difference between the diffusion under subcritical and supercritical conditions, but there is no real justification for this comparison. However, it is relevant to point out that, although supercritical fluids have in may instances greater similarity to liquids than gases, their diffusivities act more like gases in that they are inversely proportional to pressure. The diffusivities of liquids are independent of pressure. Certainly, these statements were true for the range of supercritical pressures in the reported work. Thus caging products should increase with pressure. Due to this concept, the ratio of caging intermediate methylhydroindane found for decalin compared to its  $\beta$  scission route was measured as a function of pressure at a given temperature. A substantial increase in methylhydroindane with pressure, nearly an order of magnitude increase with an increase from 1 to 85 atm in pressure was observed. These results are of great significance, not only for their application to practical considerations in that a small amount of particulates could play havoc in an aircraft gas turbine fuel line, but also that they offer fundamental confirmation of the conceptual processes proposed and illustrate the important parameters which a design engineer must consider.

### References

- 1. Shaddix, C.R., "An Experimental Study of the High Temperature Oxidation of 1-Methylnaphthalene", Princeton University, Dept. of Mech. and Aero. Eng., Ph.D. Thesis, 1993.
- 2. Emdee, J.L., Brezinsky, K., and Glassman, I., "A Kinetic Model for the Oxidation of Toluene Near 1200 K", J. Phys. Chem. <u>95</u>, 1626 (1992).

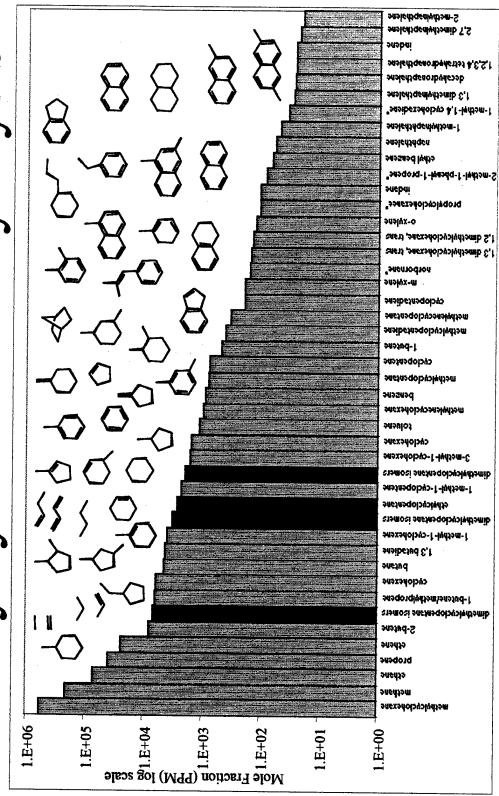
- 3. Zeppieri, S., Brezinsky, K., and Glassman, I., "Pyrolysis Studies of Methylcyclohexane and Oxidation Studies of Methylcyclohexane /Toluene Blends", Combust. Flame, 108, 266 (1997).
- 4. Glassman, I., "Fuels Combustion Research", Abstract at AFOSR Contractors Meeting, Long Beach, CA (1998).
- 5. Davis, G.T., "An Experimental Study of Supercritical Methylcyclohexane Pyrolysis", Princeton University, M.S.E. Thesis, 1994.
- 6. Stewart, J., Brezinsky, K., and Glassman, I., "Pyrolytic Formation of Polycyclic Hydrocarbons in Supercritical Methylcyclohexane", Eastern States Section/The Combustion Institute Meeting, Paper No., 1995.
- 7. Stewart, J., Brezinsky, K., and Glassman, I., "Supercritical Pyrolysis of Decane, Tetralin and n-Decane at 700-800 K: Product Distribution and Reaction Mechanism", Combust. Sci. and Tech. 136, 373 (1998).
- 8. Wu, B.C., Klein, M.T., and Sandler, S.I., "Solvent Effects on Reactions in Supercritical Fluids", Ind. Eng. Chem. Res. <u>30</u>, 822 (1991).
- 9. Glassman, I., "Combustion, 3rd Ed.", Chap. 3, Academic Press, La Jolla, CA, 1996.

## Global Kinetic Rates



# Integrated Research Summary

Fuel	Phase	A (1/sec)	Ea (kJ/mole)	Major Products
Methylcyclohexane	gas	2.55E+13	261	ethene, 1,3 butadiene, methane, propene
Methylcyclohexane	supercritical	2.51E+15	278	methane, ethane, propene, ethene, dimethylcyclopentane, propane, 1- methyl-1-cyclohexene, ethylcyclopentane.
Decalin	gas	2.70E+11	218	methane, ethene, propene, 1,3 butadiene, benzene, toluene
Decalin	supercritical	6.31E+15	276	methane, propane, ethane, propene, ethene, butene, butane, methylhexahydroindane, indene
Tetralin	supercritical	1.26E+15	273	naphthalene, <u>methylindane</u> , ethane, methane, ethene, phenylbutane, propane, propene



### Transition Under ASSERT Grant F49620-95-1-0406

Performer

I. Glassman

Customer

UTRC (Dr. M Colket)

Result

Application

Insight into sooting problem Emissions for aircraft gas turbines

Performer

I. Glassman

Customer

Rocketdyne (Dr. R. Edelman)

Result

Sooting occurrence in rocket engines

**Application** 

Emission from rocket engine

Performer

I. Glassman

Customer

SRI International (Dr. G. Faris)

Result

Carbon fiber formation

Application

Strong materials

### **Honors Award**

Propellant and Combustion Award Irvin Glassman American Institute of Aeronautics and Astronautics	1998
Distinguished Teaching Award Irvin Glassman Princeton University School of Engineering and Applied Science	1998
Election to National Academy of Engineering Irvin Glassman National Academy of Engineering	1996
Ralph Coats Roe Award Irvin Glassman American Society of Engineering Education	1984
Robt. H. Goddard Professorship Irvin Glassman Princeton University	1983
Sir Alfred Egerton Gold Medal Irvin Glassman The Combustion Institute	1982

### Principal Investigator Annual Data Collection (PIADC) Survey Form

### PI DATA

Name ONLY	Irvin Glassman	- -	AFOSR USE Project/Subarea		
Institution	Princeton University	_			
Contract/Grant	NX				
			FY		
	NUMBER OF CONTRACT/GRANT	CO-INVESTIGATORS			
Faculty	Post Doctorates	Graduate Students	_ Other _		
PUBLICATIONS RELATED TO AFOREMENTIONED CONTRACT/GRANT					
Name of Journ	nal, Book, etc.				
Combustion S	Science and Technology				
Authors J. Stew Publisher V. 136, Name of Journ	ryrolysis of Decalin, Tetralin and n-Decan anism" vart, K. Brezinsky, and I. Glassman pp. 373-390, June 1998	ie at 700-800 K. Product	Distributionand		
Authors I. Gla Publisher The Co Accept Name of Journ	ar Diffusion Flames Effect of Dilution, Adassman  ombustion Institute, Pittsburgh, PA  ed for publication (1998)	lditives, Pressure and Mi	crogravity"		
<u>Authors</u>	Combustion of Toluene-Butane Blends" z, K. Brezinsky and I. Glassman				

The Combustion Institute, Pittsburgh, PA Accepted for publication (1998)

### Name of Journal, Book, etc.

Journal of Propulsion and Power

### **Title of Article**

"Combustion Thermodynamics of Metal-Complex Oxidizer Mixtures"

### **Authors**

I. Glassman and P. Papas

### <u>Publisher</u>

American Institute of Aeronautics and Astronautics Accepted for publication (1998)

### Name of Journal, Book, etc.

Journal of Physical Chemistry

### **Title of Article**

"The Supercritical Pyrolysis of Endothermic Fuel"

### **Authors**

J. Stewart, K. Brezinsky and I. Glassman

### **Publisher**

The American Chemical Society Submitted 1998